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<p>(54) Title: POLYMERISABLE COMPOSITIONS  (57) Abstract  Highly filled, curable compositions containing a curable liquid, e.g. methyl methacrylate; 20 to 80 % by weight of a finely divided inorganic filler of defined particle size, e.g. silica; a non-functionalised polymer containing a low Tg component which is soluble in the curable liquid, e.g. a non-functionalised vinyl aromatic/conjugated diene block copolymer; and other components which disperse the filler in the curable liquid and couple the filler to the matrix can be used to produce cured composites which show improved resistance to stress induced by thermal cycling.</p>		

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## POLYMERISABLE COMPOSITIONS

This invention relates to the use of certain polymeric materials as agents for improving the thermal stability of moulded articles, to highly filled, curable compositions containing such agents suitable for moulding shaped articles and to the articles moulded therefrom.

Composites of highly filled polymeric compositions are becoming increasingly used as materials of construction, particularly for kitchen sinks, kitchen surfaces and sanitaryware, because of their attractive appearance and hard wearing properties. Fluid, curable compositions containing high volumes of finely divided fillers suitable for forming such articles have been described in British Patent No. 1 493 393. This specification describes fluid, curable compositions wherein high volumes of filler of specified particle size are dispersed in a curable material using polymeric dispersants. The use of polymeric dispersants enable compositions to be obtained containing high volumes of finely divided fillers, for example 50% by volume, which have a remarkably low viscosity enabling the compositions to be readily handled for example by pumping. This low viscosity, in turn, enables the compositions to be sold as fluid dispersions which can be readily transported to fabricators who can mould articles in inexpensive low pressure moulds. Although some sedimentation will inevitably occur on storage, the polymeric dispersant maintains the filler particles in a state of stable, deflocculation so that the sediment can be readily redispersed by mild agitation to give a dispersion in which the filler particles are substantially uniformly dispersed and will remain so whilst the composition is converted from a fluid dispersion to a fully cured composite. The presence of the polymeric dispersant, and its function of keeping the particles in a state of stable deflocculation, not only enables a low viscosity, redispersible dispersion to be obtained, but ensures that compatibility of the components is maintained as the

composition is cured so that a cured product free from cracks and flaws is obtained.

It is also possible to fabricate moulded articles which have a viscosity too high to be of practical value as transportable, low viscosity, redispersible compositions. Nevertheless, these compositions are useful where the fabrication operation is carried out at the same location as the composition is prepared and where storage and redispersion are not a problem. These compositions must also contain fillers which are properly dispersed within the curable composition to avoid problems of flocculation and cracking on polymerisation.

Although these compositions are widely used in the applications described above a small proportion of moulded articles fail prematurely in service, when subjected to thermal cycling such as experienced by a kitchen sink subjected successively to very hot and cold water. Certain polymeric materials have been indentified which when incorporated into a curable composition can imbue a moulded article formed from the curable composition with an improved thermal resilience, i.e. an improved performance in respect of the damage tolerance thermal shock test and often in respect of the thermal shock test, both of which are hereinafter described.

Some of the polymeric materials have been previously disclosed in United Kingdom Patent No 1132261 as components in curable compositions which are used to improve the impact resistance of cast articles such as tops for games tables and shop counters. However, there is no disclosure of such polymeric materials being used as agents for improving the thermal resilience of cast articles.

According to a first aspect of the present invention there is provided highly filled, curable composition comprising

- (A) an addition polymerisable organic liquid which on curing forms a solid polymer;
- (B) 20 to 80% by volume of a finely divided particulate inorganic filler having a weight average particle size of

less than 50 microns but not having a BET surface area of more than  $30\text{m}^2.\text{cm}^{-3}$ ;

- (C) a non-functionalised polymeric material which is soluble in the organic liquid but which is phase separated by the time the composition has been cured and containing at least one segment of low Tg polymeric material, optionally essentially free from unsaturation, which exhibits a Tg of less than  $0^\circ\text{C}$  and preferably less than  $-25^\circ\text{C}$ ;
- (D) a component which is capable of associating with and effecting anchoring to the particles of the inorganic filler and which provides a sufficiently large steric layer soluble in component A whereby filler particles are dispersed in the organic liquid; and
- (E) a component which will provide chemical bonding between the filler and polymer matrix formed by curing the polymerisable liquid.

Components C, D and E may be separate additive materials each providing the particular specified functions. Alternatively, more than one function may be provided in a single material, for example a single component may provide a dispersing effect and may contain a low Tg polymeric portion.

Preferred polymerisable organic liquids (A) have a viscosity below 1,000 centipoise, more preferably below 100 centipoise, as measured at ambient temperatures using a Brookfield viscometer. Particularly preferred polymerisable organic liquids have a viscosity of up to 50 centipoise. More particularly, the polymerisable organic liquid is one which cures to form a polymer having a glass transition temperature of at least  $60^\circ\text{C}$ , preferably of at least  $80^\circ\text{C}$  and more preferably of at least  $100^\circ\text{C}$ .

Preferred polymerisable organic liquids comprise at least one mono olefinically unsaturated monomer which may be selected from any of the mono olefinically unsaturated monomers known in the art.

Suitable mono olefinically unsaturated monomers may be selected from the acrylic type monomers such as acrylic, methacrylic and chloroacrylic acids (i.e.  $\text{CH}_2=\text{CHClCO.OH}$ ), acrylamide and methacrylamide, acrylonitrile and methacrylonitrile, alkoxyalkyl acrylamides and methacrylamides, e.g. butoxymethyl acrylamide and methoxymethyl methacrylamide, hydroxyalkyl acrylamides and methacrylamides, e.g. N-methylol acrylamide and methacrylamide, the metal acrylates and methacrylates, and the esters of acrylic, methacrylic and chloroacrylic acids with alcohols and phenols; the vinyl aromatic compounds, e.g. styrene and substituted derivatives thereof such as the halogenated derivatives thereof and vinyl toluene; the vinyl esters, e.g. vinyl acetate, and vinyl pyrrolidone.

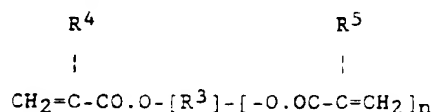
In a preferred polymerisable organic liquid, the at least one mono olefinically unsaturated monomer is an acrylic or methacrylic acid ester having the formula  $\text{CH}_2=\text{C(R)CO.OR}^2$  where R is H or methyl, especially methyl, and  $\text{R}^2$  is optionally substituted hydrocarbyl (e.g. optionally halo or hydroxy substituted hydrocarbyl) and in particular is a  $\text{C}_{1-8}$  alkyl, a  $\text{C}_6-10$  cycloalkyl or a  $\text{C}_6-10$  aryl group. Specific examples of such monomers include the non-substituted esters of acrylic and methacrylic acids such as methyl methacrylate, ethyl methacrylate, isopropyl methacrylate, isobutyl methacrylate, cyclohexyl methacrylate, isobornyl methacrylate, benzyl methacrylate, phenyl methacrylate and isobornyl acrylate and the substituted esters of acrylic and methacrylic acids such as hydroxyethyl methacrylate and hydroxypropyl methacrylate. More particularly, the mono olefinically unsaturated monomer incorporated in the polymerisable organic liquid is a  $\text{C}_{1-8}$  alkyl ester of methacrylic acid. Methyl methacrylate is an especially preferred monomer.

The polymerisable organic liquid may comprise a mixture of mono olefinically unsaturated monomers, for example a mixture of

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the mono olefinically unsaturated monomers specified as preferred above.

The preferred polymerisable organic liquids may also comprise at least one polyolefinically unsaturated monomer so that the polymer which forms on curing the polymerisable organic liquid is a cross-linked polymer. Suitable polyolefinically unsaturated monomers may be selected from those known in the art. Preferred polyolefinically unsaturated monomers are the poly(meth)acrylate esters of an organic polyol and acrylic or methacrylic acid having the formula:



wherein

$R^3$  is the hydroxy free residue of an organic polyol which comprised at least two hydroxyl groups in the molecule bonded to different carbon atoms;

$R^4$  and  $R^5$  are each independently hydrogen or methyl; and  $n$  is an integer having a value of at least 1, preferably a value of from 1 to 3.

Suitable poly(meth)acrylates of this type include, inter alia, the mono-, di-, tri- and tetra-alkylene glycol di(meth)acrylates such as 1,3-butylene glycol dimethacrylate, 1,3-butylene glycol diacrylate, ethylene glycol diacrylate, ethylene glycol dimethacrylate, triethylene glycol diacrylate, triethylene glycol dimethacrylate and tetraethylene glycol dimethacrylate, and the trialkylolalkane tri(meth)acrylates such as trimethylolpropane trimethacrylate and trimethylolpropane triacrylate. Other suitable poly(meth)acrylates may be selected from the polyalkylene glycol di(meth)acrylates, such as polyethylene glycol dimethacrylate, the bisphenol di(meth)acrylates, such as Bisphenol A dimethacrylate, and the di(meth)acrylates of the alkoxyated bisphenols, such as the dimethacrylate of an ethoxyated and/or propoxyated derivative of Bisphenol A. The poly(meth)acrylate monomer may also be an acrylated or

methacrylated epoxy resin, for example the product derived by reacting methacrylic acid with an epoxy resin which is the reaction product of a bisphenol, such as Bisphenol A, and a halohydrin, such as epichlorohydrin. Mixtures of poly(meth)acrylate monomers may be used if desired.

More particularly, the poly(meth)acrylate monomer is a mono-, di-, tri- or tetra- alkylene glycol di(meth)acrylates or a trialkylolalkane tri(meth)acrylates, especially the former. A particularly preferred poly(meth)acrylate is ethylene glycol dimethacrylate.

The polymerisable organic liquid will usually comprise (by weight) from 0.2 to 20, for example from 0.5 to 20%, more usually from 0.5 to 15%, for example from 1.0 to 15%, by weight, and preferably from 0.5 to 10%, for example from 1.0 to 10%, of the at least one polyolefinically unsaturated monomer, and usually from 99.8 to 80%, for example 99.5 to 80%, more usually from 99.5 to 85%, for example 99 to 85%, and preferably from 99.5 to 90%, for example from 99 to 90% by weight of the at least one olefinically unsaturated monomer.

However, certain polyolefinically unsaturated monomers may be employed in higher concentrations, e.g. the polyalkylene glycol di(meth)acrylates and the di(meth)acrylates of the alkoxyated bisphenol derivatives. A polymerisable organic liquid comprising such monomers may comprise up to 70% by weight thereof, e.g. up to 50% by weight.

Suitable inorganic fillers (B) may include amphoteric, basic and siliceous fillers, and may be of natural or synthetic origin. The inorganic filler, if amphoteric, may, for example, be an oxide of this type. Suitable such inorganic fillers include oxides and hydroxides of aluminium, including hydrated alumina. The inorganic filler, if basic, may, for example, be an oxide, a hydroxide, a carbonate or a basic carbonate. Suitable inorganic fillers of this type include, inter alia, the oxides, hydroxides, carbonates and basic carbonates of alkaline earth metals and of zinc. Suitable siliceous fillers include, inter



alia, substantially pure silica, for example sand, quartz, cristobalite and precipitated or fused silica, or the metal silicates or aluminosilicates. Further useful inorganic fillers may be selected from the metal aluminates, phosphates, sulphates, sulphides and carbides. Siliceous fillers are preferred, especially the silica fillers.

When the inorganic filler is to be used in a composition of the type described in British Patent Specification 1 493 393 providing a stably deflocculated redispersible dispersion the inorganic filler should be one in which the maximum size of any particle present is 100 microns, and at least 95% by number of the particles are of a size 10 microns or less, and where the particles have a surface area of from  $30 \text{ m}^2.\text{cm}^{-3}$  to  $1 \text{ m}^2.\text{cm}^{-3}$  (approximately from  $10 \text{ m}^2.\text{g}^{-1}$  to  $0.4 \text{ m}^2.\text{g}^{-1}$ ), preferably from  $20 \text{ m}^2.\text{cm}^{-3}$  to  $2 \text{ m}^2.\text{cm}^{-3}$  (approximately from  $8.5 \text{ m}^2.\text{g}^{-1}$  to  $0.8 \text{ m}^2.\text{g}^{-1}$ ), as determined by the B.E.T. nitrogen absorption method.

Preferably more than 99% by number of the particles are of a size 10 microns or less, and in general the nearer the number proportion of such particles approaches 100% the better, e.g. a proportion of 99.999% by number of a size 10 microns or less gives very satisfactory results. It is at the same time preferred that the maximum size of any particles present should be 75 microns, even more preferred that the maximum size should be 50 microns. The inorganic filler particles for use in the invention may have any form suitable for a filler, e.g. they may be of granular, fibrillar or laminar form.

In compositions having less exacting requirements, for example, where the composition is to be made up and cured in the same processing facility (in-house) and where it is not necessary to provide a dispersion which is readily pumpable from drums and which can be redispersed after storage, it is not necessary for the particle size to be so critical. For such compositions the BET particle surface area may be less than  $1 \text{ m}^2.\text{cm}^{-3}$  and, for example, the weight average particle size may be as much as

50 microns or more. The BET particle surface area should be less than  $30 \text{ m}^2.\text{cm}^{-3}$ .

Curable compositions contain from 20 to 80% by volume of the finely divided particulate inorganic filler. Preferably the concentration of the inorganic filler is from 30% to 75% by volume and more preferably from 40 to 70% by volume of the total volume of the curable composition.

Where the inorganic filler is already available in the required particle size, the particles of inorganic filler can be dispersed in the curable compositions using techniques known in the art. Mixing processes such as roll milling or high shear mixing may be used to disperse the inorganic filler. For example, the inorganic filler may be mixed with the polymerisable organic liquid or a portion thereof to form a filler/liquid mixture into which is added the copolymer dispersant, e.g. as a solution in a component of the polymerisable organic liquid, with mixing. A further suitable technique involves blending the inorganic filler in a component of the polymerisable organic liquid and then blending the resulting mixture with the remaining components of the curable composition. Alternatively, the finely divided particles may be produced directly in the presence of the curable composition, or in a liquid component thereof, by comminution of coarse particles. Comminution of coarse material to yield smaller size particles can be readily carried out using conventional ball mills, stirred ball mills or vibratory mills.

Where the dispersion need not be limited to a stably deflocculated redispersible dispersion, i.e. a level of non-redispersion can be tolerated, the inorganic filler used to produce curable compositions may also comprise a coarse filler material, e.g. a filler material the particles of which have a mean size across their largest dimension of at least 100 microns, e.g. greater than 200 microns, and typically within the range 100 to 500 microns, e.g. 200 or 300 microns. Such compositions are useful where it is required to produce a surface rich in larger

filler particles or where some special aesthetic effect such as a simulated granite effect is required.

The non-functionalised polymeric material (C) soluble in the organic liquid (A) containing at least one segment of low Tg polymeric material having a Tg of less than 0°C may consist wholly of such a low Tg polymeric material material. Alternatively, and preferably, the non-functionalised polymeric material may contain segments of such material, for example as in a block copolymer.

The term "non-functionalised" used in the present application is used in the sense that the polymeric component does not contain, particularly as pendant groups, moieties which may be used as bonding agents in respect to the inorganic filler present in the curable composition. Examples of such moieties which are absent from the non-functionalised polymeric component are silane, carboxylic acid, carboxylic anhydride, hydroxyl, ester, imide, amide, amine, epoxy and acid chloride groups. However, nitrile and other such groups may be present.

The term "essentially free from unsaturation" used in the present application is used in the sense that the aforementioned block polymers have been hydrogenated to such an extent that the original unsaturation present has been reduced to a level at which their sensitivity to oxidation is minimised. This is achieved according to US Re 27145 by reducing the unsaturation of the conjugated diene polymer block to less than 10% of the original unsaturation. Preferably, the level of unsaturation is at an insignificant level.

It is preferred that the at least one segment of low Tg polymeric material has a molecular weight (Mn) of at least 5000.

Suitable non-functionalised multi-block polymers for use as component C include vinyl aromatic/conjugated diene block copolymers and selectively hydrogenated variants thereof. The polymerised conjugated diene hydrocarbon block should preferably have an average molecular weight (Mn) of at least 20,000 whereas the polymerised monoalkenyl aromatic hydrocarbon block should

preferably have an average molecular weight of at least 2,000 and not more than 115,000. The weight percentage of the monoalkenyl aromatic block in the block copolymer is preferably less than 35% when the polymeric dispersant derived from these block copolymers is required to confer optimum resistance to thermal and mechanical shock.

Other non-functionalised polymers suitable for use as component C include acrylonitrile/conjugated diene block copolymers and selectively hydrogenated variants thereof. The copolymer should preferably contain from 20 to 50% of acrylonitrile (on a weight basis) and particularly from 25 to 45% of acrylonitrile. Suitably the copolymer may have a Mooney Viscosity at 100°C from 50 to 100, and preferably from 55 to 90.

The non-functionalised polymeric component C should be soluble in the polymerisable organic liquid but should phase separate whilst the composition is being cured so that it forms a separate phase which is present in the cured article. Component C may be present in the form of finely dispersed particles having a maximum dimension in the range from 0.01 microns to 5 microns but may also be present in the form of a co-continuous phase of material of irregular shape with a minimum dimension greater than 5 micron.

When it is desired to obtain a significant improvement in the damage tolerance test it is necessary that after the curing process the cured composition comprises the at least one segment of low Tg polymeric material in a noncross-linked state, thereby retaining its low Tg. It is generally possible to observe the presence of a low Tg component in a cured moulding using dynamic mechanical thermal analysis testing (DMTA) to provide a check that the low Tg component has not been changed during the curing process so as to lose its rubberiness.

In a second aspect of the present invention there is provided the use of a non-functionalised polymeric material as an agent to improve the thermal resilience of a moulded article manufactured from a highly filled, curable composition comprising

- (A) an addition polymerisable organic liquid which on curing forms a solid polymer;
- (B) 20 to 80% by volume of a finely divided particulate inorganic filler having a weight average particle size of less than 50 microns but not having a BET surface area of more than  $30\text{m}^2.\text{cm}^{-3}$ ;
- (C) the non-functionalised polymeric material which is soluble in the organic liquid but which is phase separated by the time the composition has been cured and containing at least one segment of low Tg polymeric material, optionally essentially free from unsaturation, which exhibits a Tg of less than  $0^\circ\text{C}$  and preferably less than  $-25^\circ\text{C}$ ; and optionally
- (D) a component which is capable of associating with and effecting anchoring to the particles of the inorganic filler and which provides a sufficiently large steric layer soluble in component A whereby filler particles are dispersed in the organic liquid; and/or
- (E) a component which will provide chemical bonding between the filler and polymer matrix formed by curing the polymerisable liquid.

The component D comprises an amphipathic material in the sense that molecules of the material contain two distinct portions, a portion which is capable of associating with and effecting anchoring to the filler particles B, and a portion soluble in component A and having a sufficiently large steric volume in component A to achieve dispersion of the filler particles in component A.

Typically useful variations of component D are extensively described in British Patent Specification No. 1493393. The latter describes dispersing agents which are amphipathic substances containing (a) at least one chain-like component of molecular weight at least 500 which is solvated by the polymerisable organic liquid (A) and is also solvated by, or is compatible with, the oligomeric or polymeric products which result throughout the course of the curing operation from the

polymerisable organic liquid, and (b) one or more groupings which are capable of associating with, and effecting anchoring to the particles of the inorganic filler (B). The chain-like component is solvated by the polymerisable organic liquid or its curing products in the sense that, if this component were an independent molecule, the polymerisable organic liquid or those products would be significantly better than theta-solvents for it; the nature of a theta-solvent is discussed in "Polymer Handbook" (ed. Brandrup and Immergut, Interscience, 1966) and in "Principles of Polymer Chemistry, Chapters 12-14 (Flory: Cornell, 1953). More simply, the polymerisable organic liquid may be described as being a "good" solvent for the chain-like component.

The component D may itself contain a component which will effect a strong bond between the filler particles and the matrix, i.e. couple the filler particles and the matrix. Alternatively, a further separate component, E, may be included to provide this function.

The particular type of coupling or bonding agent to be used will depend upon the nature of the inorganic filler and of the polymerisable organic liquid. Suitable bonding agents are in general substances containing groups which can form a multiplicity of ionic, covalent or hydrogen bonds with the particle, and also groups which can react to form bonds with the polymer matrix. Suitable groups for bonding to particles having hydroxylic, metal oxide or siliceous surfaces are, for example, the oligomeric hydrolysis products of alkoxy silanes, chlorosilanes and alkyl titanates as well as the trivalent chromium complexes or organic acids. Where the particle surface is of a basic character, as for example in the case of particles of alkaline earth metal carbonates or of metals such as aluminium, chromium and steel, suitable bonding groups are carboxylic acid groups. In the case of particles with acidic surfaces, such as those of kaolin, amine salt groups are suitable for bonding to the particles.

Groups suitable for bringing about bonding with the polymer matrix are typically those which co-react with the polymerisable organic liquid during the polymerisation stage. Thus an interfacial bonding agent containing an ethylenically unsaturated group is suitable for use with addition polymerisation systems involving vinyl, vinylidene and similar unsaturated monomers. An agent containing an amino, an oxirane or a carboxyl group is suitable for use with epoxy-group-containing compounds. Examples of suitable interfacial bonding agents include:

- gamma-methacryloxypropyl trimethoxy silane
- gamma-aminopropyl trimethoxysilane
- gamma-glycidyloxypropyl trimethoxysilane
- vinyl triethoxysilane
- vinyl triacetoxysilane
- vinyl trichlorosilane
- Acrylic and methacrylic acids and their metal salts
- Methacrylatochromic chloride
- Maleimidopropionic acid
- Succinimidopropionic acid
- 4-Amonimethylpiperidine
- Tetraisopropyl and tetrabutyl titanates

The amounts of the interfacial bonding agent used are, in general those conventional in the art of polymeric materials reinforced with inorganic fillers. A suitable minimum usage for most applications is 0.001g of bonding agent per square metre of filler particle surface area. If desired, a mixture of two or more interfacial bonding agents of the types described may be used.

Curable compositions may also comprise one or more preformed polymers which may be in solution in the polymerisable organic liquid, for example, a partially polymerised syrup of the polymerisable organic liquid. Alternatively they may be present in a state of dispersion therein. Preformed polymers may also be included as a thickening aid to adjust the viscosity of the curable compositions.

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Curable compositions may also comprise any of the additives that are conventionally used in curable moulding compositions such as pigments, dyestuffs, mould release agents and polymerisation inhibitors.

Curable compositions are usefully employed in the manufacture of moulded articles. Fluid curable compositions having a low viscosity obtainable using the dispersants of the invention are particularly suitable for moulding applications and, accordingly preferred curable compositions will have a viscosity, as measured when the filler is dispersed in the polymerisable organic liquid, of less than 5000 centipoise at ambient temperatures. More particularly, compositions having a viscosity, as measured when the filler is so dispersed, in the range of from 50 to 2000 centipoise and especially in the range of from 50 to 1000 centipoise are preferred.

In a third aspect of the present invention there is provided a moulded article formed by curing the curable composition of the first aspect of the invention.

Moulded articles may be fabricated using techniques conventional in the art. For example, the curable composition can be cast into a mould and then in-mould polymerised using a suitable catalyst to initiate the polymerisation reaction.

The polymerisable compositions may be cured in accordance with techniques conventional in the art of free radical addition polymerisation. The polymerisation may be initiated by a wide range of catalysts, but it is preferred to use a heat activated catalyst, particularly one which is activated at temperatures of from 30 to 120°C. The catalyst is preferably added immediately prior to curing the compositions; this may be particularly important where the catalyst is activated at temperatures below or around ambient. Suitable catalysts are well known to those skilled in the art and may include, for example, organic peroxides, such as dibenzoyl peroxide, diocatanoyl peroxide and di-t-butyl peroxide, which may be used in conjunction with an amine accelerator, e.g. N,N-diethylaniline or



N,N-dimethyl-para-toluidine; the hydroperoxides, such as t-butyl hydroperoxide; the peroxydicarbonates, such as diisopropylperoxydicarbonate, di-n-propylperoxydicarbonate, di-(2-ethoxyethyl)-peroxydicarbonate, di-(methoxyisopropyl)-peroxydicarbonate, di-(2-ethylhexyl)-peroxydicarbonate and bis(4-t-butylcyclohexyl)peroxydicarbonate; and the peresters. The most preferred catalysts are the peroxydicarbonates. The catalyst is conveniently used in an amount ranging from 0.1% to 3.5% by weight based on the total weight of the polymerisable organic liquid.

It may be desirable during the filling of the mould to maintain the temperature of the mould surfaces below the temperature at which the catalyst is activated, so as to prevent premature polymerisation and gelation.

Prior to moulding, the internal mould surfaces may be coated with a release agent to prevent adhesion of the cured materials to the mould and to obtain a good surface finish. These techniques are well known in the art. Examples of suitable external mould release agents include, inter alia, polytetrafluoroethylene, silicone and polyvinylalcohol.

After the in-mould polymerisation is complete, the filled polymeric article may be subjected to an in-mould post-curing process, after which it is demoulded, or, alternatively, it may be demoulded immediately and then optionally subjected to a post-curing process.

The invention is further illustrated by reference to the following examples.

In the examples unless otherwise stated, the cristobalite silica that was used had a mean weight particle size of 10 microns.

Also, the viscosity was measured on a Brookfield viscometer using a No. 3 spindle at 30 rpm.

Likewise, the dispersions were cured in the form of plaques (dimensions 300 mm x 300 mm x 5 mm) and kitchen sinks after catalysing with 0.6% by weight of the dispersion of Perkadox 16

catalyst (bis(4-t-butyl-cyclohexyl) peroxydicarbonate) (available from Akzo) using the appropriate moulds. The curing cycle for moulding plaques was 30 minutes at 60°C followed by 45 minutes at 90°C. The curing cycle for moulding sinks was 80°C on show face and 50°C on back face for 15 minutes, followed by 100°C on show face and 100°C on back face for 15 minutes, the moulding pressure was held at 2 bar for 10 minutes followed by 4.5 bar for 20 minutes.

The plaques were cut into test pieces for measurement of modulus, failure stress, failure strain and impact strength. The test methods were three point bend flexural test, ASTM D790-71 and the Charpy unnotched impact test, ASTM D256 Method B.

The thermal shock performance of the moulded sinks were assessed by the following method. Hot and cold water were alternately, and repeatedly, jetted onto the base of the sink; the sink was continually observed and the number of cycles to failure or damage was measured. Each heating and cooling cycle was as follows: hot water at  $93^{\circ}\text{C} \pm 2^{\circ}\text{C}$  was jetted onto the base of the sink for 90 seconds, followed by a dwell time of 30 seconds during which time there was no flow of water, then cold water  $15^{\circ}\text{C} \pm 5^{\circ}\text{C}$  was jetted onto the base of the sink for 90 seconds, followed by a further dwell time of 30 seconds.

The damage tolerance thermal shock test involved using the same heating and cooling cycle described above, but the sink was scratched by drawing a device in which a 'Stanley Knife Blade' was protruding by 1 mm from a flat surface across the show surface of the base of the sink. A scratch of length 2.5 cm was made at the point of impingement of the water jet. The sinks were observed during the thermal cycling and cycles to failure or damage were recorded.

#### Comparative Example A

The following ingredients were mixed into 25 litre drums and rolled at approximately 30 rpm for 24 hours.

Methyl methacrylate	8.03 kg
Ethylene glycol dimethacrylate	0.092 kg

Polymeric dispersant (95:5 methyl methacrylate : dimethylamino ethyl methacrylate, Mw 50,000 (GPC)	0.21 kg
Polymethyl methacrylate Mw 500,000 (GPC)	0.18 kg
Stearic acid	0.045 kg
Cristobalite silica	22 kg

A free flowing dispersion was obtained having a viscosity of 410 centipoise.

The dispersions were moulded and cured into a plaque and sinks. The plaque was cut into specimens for mechanical property determination. The values measured are recorded below:

Modulus	GPa	12.8
Failure Stress	MPa	64
Failure Strain	%	0.5
Impact Strength	kJ.m <sup>-2</sup>	2.0

Sinks were tested in the thermal shock test and failed on average (4 tests) after 50 cycles.

In the damage tolerance thermal shock test no minor damage was observed before catastrophic failure at 30 cycles.

#### Comparative Example B

The following ingredients were mixed into 25 litre drums and rolled at approximately 30 rpm for 24 hours.

Methyl methacrylate	8.03 kg
Ethylene glycol dimethacrylate	0.092 kg
Polymeric dispersant (95:5 methyl methacrylate : dimethylamino ethyl methacrylate, Mw 50,000(GPC)	0.21 kg
Polymethyl methacrylate Mw 500,000 (GPC)	0.18 kg
3-(trimethoxysilyl)propylmethacrylate	0.022 kg
Stearic acid	0.045 kg
Cristobalite silica	22 kg

A free flowing dispersion was obtained having a viscosity of 410 centipoise.

The dispersions were moulded and cured into a plaque and sinks. The plaque was cut into specimens for mechanical property determination. The values measured are recorded below.

Modulus	GPa	12.5
Failure Stress	MPa	115
Failure Strain	%	1.0
Impact Strength	$\text{kJ.m}^{-2}$	5.0

Sinks were tested in the thermal shock test and failed on average (>25 tests) after 700 cycles.

In the damage tolerance thermal shock test no minor damage was observed before catastrophic failure occurred at 30 cycles.

#### Example 1

The following ingredients were mixed into 25 litre drums and rolled at approximately 30 rpm for 24 hours.

Methyl methacrylate	8.72 kg
Ethylene glycol dimethacrylate	0.08 kg
Kraton G-1652	0.69 kg
- a styrene/ethylene/butadiene/styrene block copolymer available from the Shell Chemical Company	
Polymeric dispersant (95:5 methyl methacrylate : dimethylamino ethyl methacrylate, Mw 50,000 (GPC)	0.20 kg
3-(trimethoxysilyl)propylmethacrylate	0.080 kg
Stearic acid	0.045 kg
Cristobalite silica	20 kg

A free flowing dispersion was obtained having a viscosity of 760 centipoise.

The dispersions were moulded and poured into a plaque and sinks. The plaque was cut into specimens for mechanical property determination. The values measured are recorded below:

Modulus	GPa	11.2
Failure Stress	MPa	101
Failure Strain	%	1.3
Impact Strength	$\text{kJ.m}^{-2}$	5.0

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In the damage tolerance thermal shock test minor damage was observed at 143 cycles, and failure occurred at 256 cycles.

Comparative Example C

The following ingredients were mixed into 25 litre drums and rolled at approximately 30 rpm for 24 hours.

Methyl methacrylate	13.123 kg
Ethylene glycol dimethacrylate	0.092 kg
Polymeric dispersant (95:5 methyl methacrylate : dimethylamino ethyl methacrylate, Mw 50,000 (GPC)	0.22 kg
Polymethyl methacrylate Mw 500,000 (GPC)	1.210 kg
3-(trimethoxysilyl)propylmethacrylate	0.022 kg
Cristobalite silica	22 kg

A free flowing dispersion was obtained having a viscosity of 400 centipoise.

The dispersions were moulded and cured into a plaque and sinks. The plaque was cut into specimens for mechanical property determination. The values measured are recorded below:

Modulus	GPa	8.6
Failure Stress	MPa	112
Failure Strain	%	1.5
Impact Strength	kJ.m <sup>-2</sup>	6.0

Sinks were tested in the thermal shock test and failed on average after 1450 cycles.

In the damage tolerance thermal shock test no minor damage was observed before catastrophic failure at 50 cycles.

Example 2

The procedure of Comparative Example C was followed using a composition containing a non-functionalised soluble polymeric material and with the following ingredients:

Methyl methacrylate	47.81 kg
Ethylene glycol dimethacrylate	0.4 kg
ABA block copolymer of styrene/butadiene/styrene having a styrene content of 28% w/w and	4.0 kg

a solution viscosity (25% w/w in toluene)  
of 4000 cP at 25°C

Polymeric dispersant (95:5 methyl methacrylate : dimethylamino ethyl methacrylate, Mw 50,000 (GPC)	0.8 kg
3-(trimethoxysilyl)propylmethacrylate	0.32 kg
Cristobalite silica	80 kg

A free flowing dispersion was obtained having a viscosity of 400 centipoise.

The dispersions were moulded and cured into a plaque and sinks. The plaque was cut into specimens for mechanical property determination. The values measured are recorded below:

Modulus	GPa	7.2
Failure Stress	MPa	117
Failure Strain	%	2.3
Impact Strength	kJ.m <sup>-2</sup>	7.3

Sinks were tested in the thermal shock test and failed on average after 790 cycles.

In the damage tolerance thermal shock test, minor damage occurred at 46 cycles and failure at 109 cycles.

### Example 3

The procedure of Example 2 was followed using a composition containing a non-functionalised soluble polymeric material and with the following ingredients:

Methyl methacrylate	47.81 kg
Ethylene glycol dimethacrylate	0.4 kg
Branched styrene/butadiene copolymer	4.0 kg
having a styrene content of 30% w/w and a solution viscosity (25% w/w in toluene) of 20000 cP at 25°C	
Polymeric dispersant (95:5 methyl methacrylate : dimethylamino ethyl methacrylate, Mw 50,000 (GPC)	0.8 kg
3-(trimethoxysilyl)propylmethacrylate	0.32 kg
Cristobalite silica	80 kg

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A free flowing dispersion was obtained having a viscosity of 550 centipoise.

The dispersions were moulded and cured into a plaque and sinks. The plaque was cut into specimens for mechanical property determination. The values measured are recorded below:

Modulus	GPa	5.6
Failure Stress	MPa	109
Failure Strain	%	3.2
Impact Strength	kJ.m <sup>-2</sup>	9.1

Sinks were tested in the thermal shock test and failed on average after 743 cycles.

In the damage tolerance thermal shock test, minor damage occurred at 70 cycles and failure at 210 cycles.

#### Example 4

The procedure of Example 2 was followed using a composition containing a non-functionalised soluble polymeric material and with the following ingredients:

Methyl methacrylate	48.997 kg
Ethylene glycol dimethacrylate	0.417 kg
acrylonitrile/butadiene copolymer containing 28% acrylonitrile and having a Mooney Viscosity of 60 at 100°C	2.8 kg
Polymeric dispersant (95:5 methyl methacrylate : dimethylamino ethyl methacrylate, Mw 50,000 (GPC)	0.8 kg
3-(trimethoxysilyl)propylmethacrylate	0.32 kg
Cristobalite silica	80 kg

A free flowing dispersion was obtained having a viscosity of 480 centipoise.

The dispersions were moulded and cured into a plaque and sinks. The plaque was cut into specimens for mechanical property determination. The values measured are recorded below:

Modulus	GPa	7.8
Failure Stress	MPa	122

Failure Strain	I	2.3
Impact Strength	$\text{kJ.m}^{-2}$	6.8

Sinks were tested in the thermal shock test and failed on average after 1980 cycles.

In the damage tolerance thermal shock test, minor damage occurred at 80 cycles and failure at 200 cycles.

#### Example 5

The procedure of Example 4 was followed except that the acrylonitrile/butadiene copolymer contained 33% acrylonitrile and had a Mooney Viscosity of 60 at 100°C.

A free flowing dispersion was obtained having a viscosity of 430 centipoise.

The dispersions were moulded and cured into a plaque and sinks. The plaque was cut into specimens for mechanical property determination. The values measured are recorded below:

Modulus	GPa	6.8
Failure Stress	MPa	123
Failure Strain	I	2.6
Impact Strength	$\text{kJ.m}^{-2}$	6.9

Sinks were tested in the thermal shock test and failed on average after 3800 cycles.

In the damage tolerance thermal shock test, minor damage occurred at 60 cycles and failure at 210 cycles.

#### Example 6

The procedure of Example 4 was followed except that the acrylonitrile/butadiene copolymer contained 36% acrylonitrile and had a Mooney Viscosity of 60 at 100°C.

A free flowing dispersion was obtained.

The dispersions were moulded and cured into a plaque and sinks. The plaque was cut into specimens for mechanical property determination. The values measured are recorded below:

Modulus	GPa	6.8
Failure Stress	MPa	125
Failure Strain	I	2.3
Impact Strength	$\text{kJ.m}^{-2}$	7.6



Sinks were tested in the thermal shock test and failed on average after 1320 cycles.

In the damage tolerance thermal shock test, minor damage occurred at 150 cycles and failure at 280 cycles.

Example 7

The procedure of Example 4 was followed except that the acrylonitrile/butadiene copolymer contained 36% acrylonitrile and had a Mooney Viscosity of 80 at 100°C.

A free flowing dispersion was obtained.

The dispersions were moulded and cured into a plaque and sinks. The plaque was cut into specimens for mechanical property determination. The values measured are recorded below:

Modulus	GPa	6.7
Failure Stress	MPa	125
Failure Strain	%	2.6
Impact Strength	$\text{kJ.m}^{-2}$	7.8

Sinks were tested in the thermal shock test and failed on average after 950 cycles.

Example 8

The procedure of Example 4 was followed except that the acrylonitrile/butadiene copolymer contained 41% acrylonitrile and had a Mooney Viscosity of 80 at 100°C.

A free flowing dispersion was obtained having a viscosity of 370 centipoise.

The dispersions were moulded and cured into a plaque and sinks. The plaque was cut into specimens for mechanical property determination. The values measured are recorded below:

Modulus	GPa	7.6
Failure Stress	MPa	107
Failure Strain	%	1.7
Impact Strength	$\text{kJ.m}^{-2}$	5.6

Sinks were tested in the thermal shock test and failed on average after 950 cycles.

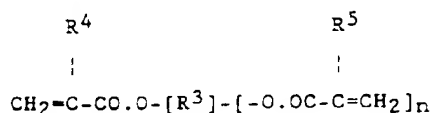
In the damage tolerance thermal shock test, minor damage occurred at 100 cycles and failure at 300 cycles.

## CLAIM

1. A highly filled, curable composition comprising
  - (A) an addition polymerisable organic liquid which on curing forms a solid polymer;
  - (B) 20 to 80% by volume of a finely divided inorganic particulate filler having a weight average particle size of less than 50 microns but not having a BET surface area of more than  $30\text{m}^2.\text{cm}^{-3}$ ;
  - (C) a non-functionalised polymeric material soluble in the organic liquid but which is phase separated by the time the composition has been cured and containing at least one segment of low Tg polymeric material, optionally essentially free from unsaturation, which exhibits a Tg of less than  $0^\circ\text{C}$ ;
  - (D) a component which is capable of associating with and effecting anchoring to the particles of the inorganic filler and which provides a sufficiently large steric layer soluble in component A whereby filler particles are dispersed in the organic liquid; and
  - (E) a component which will provide chemical bonding between the filler and polymer matrix formed by curing the polymerisable organic liquid.
2. A curable composition as claimed in claim 1 wherein the polymerisable organic liquid (A) is one which cures to form a solid polymer having a glass transition temperature of at least  $60^\circ\text{C}$ .
3. A curable composition as claimed in either claim 1 or claim 2 wherein the polymerisable organic liquid (A) comprises at least one mono olefinically unsaturated monomer which is an acrylic or methacrylic acid ester having the formula  $\text{CH}_2=\text{C}(\text{R})\text{CO}.\text{OR}^2$  where R is H or methyl and  $\text{R}^2$  is optionally substituted hydrocarbyl.
4. A curable composition as claimed in any one of claims 1 to 3 wherein the polymerisable organic liquid (A) comprises at least one polyolefinically unsaturated monomer so that the polymer

which forms on curing the polymerisable organic liquid is a cross-linked polymer.

5. A curable composition as claimed in claim 4 wherein the least one polyolefinically unsaturated monomer is a poly(meth)acrylate ester of an organic polyol and (meth)acrylic acid having the formula:



wherein

$\text{R}^3$  is the hydroxy free residue of an organic polyol which comprised at least two hydroxyl groups in the molecule bonded to different carbon atoms;

$\text{R}^4$  and  $\text{R}^5$  are each independently hydrogen or methyl; and

$n$  is an integer having a value of at least 1, preferably a value of from 1 to 3.

6. A curable composition as claimed in either claim 4 or claim 5 wherein the polymerisable organic liquid (A) comprises from 0.2 to 20% by weight of the at least one polyolefinically unsaturated monomer and from 99.8 to 80% by weight of the at least one mono olefinically unsaturated monomer.

7. A curable composition as claimed in any one of claims 1 to 6 wherein the inorganic filler (B) is at least one amphoteric, basic or siliceous filler.

8. A curable composition as claimed in any one of claims 1 to 7 further comprising a coarse filler material.

9. A curable composition as claimed in any one of claims 1 to 8 wherein the at least one segment of low  $T_g$  polymeric material is essentially free from unsaturation.

10. A curable composition as claimed in any one of claims 1 to 9 wherein the non-functionalised polymeric material comprises polymer segments which do not have a  $T_g$  of less than 0°C.

11. A curable composition as claimed in any one of claims 1 to 10 wherein the at least one segment of low  $T_g$  polymeric material has a molecular weight ( $M_n$ ) of at least 5000.

12. A curable composition as claimed in any one of claims 1 to 11 wherein the non-functionalised polymeric material is a vinyl aromatic/conjugated diene or acrylonitrile/conjugated diene block copolymer.
13. A curable composition as claimed in any one of claims 1 to 12 wherein the non-functionalised polymeric material is in the form of finely dispersed particles having a maximum dimension from 0.1 microns to 5 microns.
14. A curable composition as claimed in any one of claims 1 to 12 wherein the non-functionalised polymeric material is in the form of a co-continuous phase of material of irregular shape with a minimum dimension greater than 5 microns.
15. A curable composition as claimed in any one of claims 1 to 14 wherein the component (D) also contains a component (E) which will provide chemical bonding between the filler and polymer matrix formed by curing the polymerisable organic liquid.
16. A highly filled, curable composition comprising
- (A) an addition polymerisable organic liquid comprising a mixture of methyl methacrylate and ethylene glycol dimethacrylate;
  - (B) a finely divided inorganic particulate filler comprising cristobalite silica having a weight average particle size of less than 50 microns but not having a BET surface area of more than  $30\text{m}^2.\text{cm}^{-3}$ ;
  - (C) a non-functionalised polymeric material soluble in the organic liquid but which is phase separated by the time the composition has been cured and containing at least one segment of low Tg polymeric material which exhibits a Tg of less than  $0^\circ\text{C}$ , and comprising a non-functionalised acrylonitrile/conjugated diene block copolymer;
  - (D) 3-(trimethoxysilyl)propylmethacrylate.
17. A cured composition prepared from a curable composition as claimed in any one of claims 1 to 16.

18. A cured composition as claimed in claim 16 wherein the at least one segment of low Tg polymeric material is present in a noncross-linked state.

19. Use of a non-functionalised polymeric material as an agent to improve the thermal resilience of a moulded article manufactured from a highly filled, curable composition comprising

- (A) an addition polymerisable organic liquid which on curing forms a solid polymer;
- (B) 20 to 80% by volume of a finely divided particulate inorganic filler having a weight average particle size of less than 50 microns but not having a BET surface area of more than  $30\text{m}^2.\text{cm}^{-3}$ ;
- (C) the non-functionalised polymeric material which is soluble in the organic liquid but which is phase separated by the time the composition has been cured and containing at least one segment of low Tg polymeric material, optionally essentially free from unsaturation, which exhibits a Tg of less than  $0^\circ\text{C}$ ; and optionally
- (D) a component which is capable of associating with and effecting anchoring to the particles of the inorganic filler and which provides a sufficiently large steric layer soluble in component A whereby filler particles are dispersed in the organic liquid; and/or
- (E) a component which will provide chemical bonding between the filler and polymer matrix formed by curing the polymerisable liquid.

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 92/02081

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) * According to International Patent Classification (IPC) or to both National Classification and IPC IPC <sup>5</sup> : C 08 L 33/12, C 08 L 33/04		
<b>II. FIELDS SEARCHED</b> Minimum Documentation Searched * Classification System   Classification Symbols IPC <sup>5</sup>   C 08 L 33/00, C 08 F 2/00, C 08 K Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> *		
Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages **	Relevant to Claim No. **
X	US, A, 4 826 901 (ITTMANN et al.) 02 May 1989 (02.05.89), see totality.	1-9, 15-19
Y	EP, A2, 0 295 005 (IMPERIAL INDUSTRIES PLC) 14 December 1988 (14.12.88), see pages 2-3, line 53; page 5, line 52 - page 6, line 21; examples; claims.	1-19
Y	US, A, 4 598 123 (CUTTER) 01 July 1886 (01.07.86), see column 2, line 57 - column 5, line 5; examples; claims.	1-19
Y	EP, A2, 0 390 385 (IMPERIAL CHEMICAL INDUSTRIES PLC) 03 October 1990	1-19
* Special categories of cited documents: ** "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such docu- ments, such combination being obvious to a person skilled in the art "Z" document member of the same patent family		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search 15 January 1993		Date of Mailing of this International Search Report 03.02.93
International Searching Authority EUROPEAN PATENT OFFICE		Signature of Authorized Officer TENGLER e.h.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
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A	<p>(03.10.90), see pages 2-4, line 2; examples; claims. --</p> <p>US, A, 4 251 576 (OSBORN et al.) 17 February 1981 (17.02.81), see examples; claims &amp; GB, A, 1 493 393 (cited in the application). ----</p>	1-19

## ANHANG

zum internationalen Recherche-  
bericht über die internationale  
Patentanmeldung Nr.

## ANNEX

to the International Search  
Report to the International Patent  
Application No.

## ANNEXE

au rapport de recherche inter-  
national relatif à la demande de brevet  
international n°

PCT/GB92/02081 SAE 66403

In diesem Anhang sind die Mitglieder  
der Patentfamilien der in obenge-  
nannten internationalen Recherchebericht  
angeführten Patentdokumente angegeben.  
Diese Angaben dienen nur zur Unter-  
richtung und erfolgen ohne Gewähr.

This Annex lists the patent family  
members relating to the patent documents  
cited in the above-mentioned inter-  
national search report. The Office is  
in no way liable for these particulars  
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La présente annexe indique les  
membres de la famille de brevets  
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